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Report 682-Final

1 November 1960 - 31 January 1961

FUNDAMENTAL CORROSION RESEARCH

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Department of Metallurgical Engineering

Office of Naval Research
Contract Nonr-495(11)
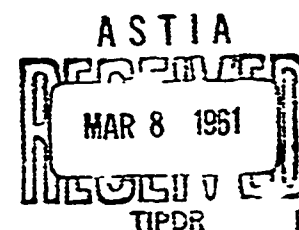
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R E P O R T

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Columbus 12, Ohio

To: OFFICE OF NAVAL RESEARCH
                Contract Nonr-495(11)
                Project NR 036-006/10-24/55

On.   FUNDAMENTAL CORROSION RESEARCH

For the period: 1 November 1960 - 31 January 1961

Submitted by: M. G. Fontana and F. H. Beck
               Department of Metallurgical Engineering

Date: 31 January 1961

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FUNDAMENTAL CORROSION STUDIES

INTRODUCTION

The significant and completed investigations conducted under Contract Nonr-495(11) during the period February 1, 1956, through January 31, 1961, have been published and presented as technical reports.

A limited but informative investigation of pitting corrosion appears in Report Nos. 17 and 18 and is summarized in Report No. 19.

Part I of this report includes a detailed discussion of the completed study of stress-corrosion cracking of the magnesium-base, J-1, alloy. Part II presents a summary of the incompleted work on the stress corrosion of austenitic stainless steel by 400°F chloride containing waters and, in particular, the role of corrosion product in the stress-corrosion mechanism.

A list of the quarterly reports and technical publications resulting under this study is shown in the back of this report.

PART I. STRESS CORROSION CRACKING OF MAGNESIUM-BASE ALLOY, J-1, BY SALT-CHROMATE SOLUTION

A. INTRODUCTION

Stress-corrosion is cracking that occurs under the combined action of a tensile stress and a corrosive medium which is ordinarily selective in its attack of the metal. Considerable amounts of work have been directed toward understanding the mechanisms involved in this phenomenon. It is generally accepted that intergranular failure is an electrochemical process, but the mechanism of transgranular failure is uncertain

This investigation was undertaken to study the stress-corrosion of a magnesium-6% aluminum-1% zinc alloy in a sodium chloride-potassium chromate solution. A considerable amount of work has been done on this alloy, primarily because it can conveniently be made to fail in either a transgranular or intergranular manner and in a short time.

The effects of iron content, heat treatment, and grain size are the most important subjects investigated. Corrosion currents in both transgranular and intergranular stress-corrosion are discussed. Microscopic examinations and sound pickup apparatus were utilized as well. The effects of stress level, mechanical properties, time under load, pH, and surface treatment are also discussed.

B. SUMMARY AND CONCLUSIONS

A study of the stress-corrosion cracking of a magnesium-6% aluminum-1% zinc alloy was made in a salt-chromate solution. A motion picture of the stress-corrosion process was filmed.

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The conclusions drawn from this investigation are as follows:

a. Transgranular stress-corrosion takes place by a mechanism which consists of alternate steps of electrochemical and mechanical actions. Corrosion current measurements, crack advance rates, and associated sound levels are all discontinuous. Material which is susceptible to transgranular failure is inherently more brittle. All of these facts indicate that transgranular failure is a brittle, discontinuous, and predominantly mechanical process. A mechanism is proposed whereby electrochemical attack initiates cracking but brittle mechanical failure causes most of the destructive action.

b. Stress-corrosion currents are roughly proportional to the applied stress in the plastic range.

c. Uniformity of surface preparation is a critical factor in the reproducibility of corrosion current measurements. Incomplete preparation results in a more complex electrochemical system.

d. Higher iron content, larger grain size, and water quenching all promote transgranular attack. It is believed that these effects are all associated with a blocking of dislocation movement by a $FeAl$ precipitate within the grains which promotes brittle mechanical failure.

e. Intergranular attack is associated with the formation of $Mg_{17}Al_{12}$ at grain boundaries. This precipitate is promoted by furnace cooling from solution heat treatment temperatures.

f. The effect of pH has no effect on whether stress corrosion is transgranular or intergranular when specimens with large grain sizes are used. Large grained specimens always fail in a transgranular manner.

g. Specimens which are stressed for long periods of time under conditions which prevent formation of a surface film do not fail when exposed to the salt-chromate solution. This effect is attributed to stress relaxation associated with creep.

h. The characteristics of the two types of failure are the same regardless of whether constant load or constant deflection techniques of stressing are used.

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C. PROCEDURE AND APPARATUS

1. Preparation of Specimens

All material used in this investigation of stress corrosion was the magnesium-base alloy designated Dowmetal J-1 or ASTM Alloy No. A2611. The alloy was donated by the Dow Chemical Company. Two production lots were used, with compositions as shown in Table 1. It may be noted that the only appreciable differences are the higher aluminum and iron contents of Lot No. 44.

In all cases except where noted, specimens $3/16 \times 3/16 \times 4$-$1/2$ inches were machined from a rectangular extruded bar with an original cross-section of $1/4 \times 3/4$ inch. No prior heat treatment was utilized.

Solution-anneal heat treatments were given all specimens. Heat treatments consisted of heating at 650, 800, or 900°F for 24 hours followed by furnace cooling or quenching in water. The 800°F treatment was utilized to obtain large grains. The 900°F treatment was used in conjunction with a prior cold-working operation of 5% reduction in area by longitudinal rolling and produced single crystals or bi-crystals across the width of the specimens. Specimens for both the 800 and 900°F heat treatments were sealed in Pyrex glass capsules to prevent excessive oxidation.

Metallographic preparation of the specimens for microscopic examination was as follows. The specimens were abraded on 240, 400, and 600 grit silicon carbide papers. The specimens were then washed and initially polished on a medium speed wheel with Linde "B" on a Buehler Kitten Ear polishing cloth using water as a lubricant. Final polishing was done on a medium speed wheel with MgO on a Buehler Microcloth, again

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using water as a lubricant. The specimens were etched with a modified picric-acetic etch composed of 6 g picric acid, 150 ml ethanol, 18 ml acetic acid, and 17 ml of distilled water.

2. Experimental Apparatus

The experimental apparatus used in this investigation is shown in Fig. 1. Unless otherwise indicated, all specimens were stressed in a holder constructed of synthane, an electrically insulating material. A pictorial representation of a specimen mounted in the holder is shown in Fig. 2. The distance between the end supports of the specimen holder is four inches. The stress in the outer fibers of the specimen at the point of maximum stress is proportional to the amount of deflection. An approximate value of stress is calculated from the equation:

$$S = \frac{12yEC}{L^2}$$

where S is the stress, y is the deflection in inches, E is Young's modulus, C is half the specimen width and L is the specimen length in inches.

After stressing, the specimen and holder were placed in a container of the corrosive medium which was attached to a micrometer traveling stage under the microscope. Electrical connections for the measurement of corrosion currents generated between the stressed specimen (anode) and an unstressed specimen of the J-1 alloy (cathode) are shown in Fig. 2. The microscope permitted either direct visual observation or motion picture microscopy to be used.

In addition, a commercially available sound detection unit was used to record the sounds of the stress-corrosion process. The unit consisted of a 1/4-inch diameter metallic probe 10 inches long, a crystal

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microphone which was permanently attached to one end of the probe, and a high-gain, low-noise amplifier. The tip of the probe was in contact with the specimen and the output of the amplifier was recorded on a commercial Webcor tape recorder or a motion picture sound track, as desired.

The corrosive medium was usually a sodium chloride-potassium chromate solution (pH = 9) consisting of 40 grams of NaCl and 40 grams of K_2CrO_4 per liter of water. The one exception was a solution of 35 grams sodium chloride and 20 grams of potassium dichromate per liter of water (pH = 3.5) which was used to determine the effect of pH value on type of stress-corrosion failure.

3. Experimental Procedures

    a. <u>Study of Metallurgical Structure</u>

    Specimens from both production lots of the J-1 alloy were prepared metallographically and examined microscopically to determine the structure of the alloy in the as-received condition. Similar examinations were made after heat treating at the 650, 800, and 900°F temperatures followed by either furnace cooling or quenching in water. These specimens were exposed under standard test conditions to determine the type of failure.

    b. <u>Resolution of Sound Associated</u>
        <u>With the Cracking Process</u>

    An audio pickup was utilized to determine if any sound was associated with the cracking process of the alloy. In addition, it was attempted to determine the exact cause of the sound * to correlate this with a mechanism of crack propagation. These noise determinations were made on all runs.

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c. Evaluation of Changes in Electrical Resistance

Several attempts were made to determine the distance of crack penetration by measurements of change in specimen resistance.

d. Measurements of Corrosion Current
as an Experimental Method

Corrosion currents were measured in the manner explained earlier between stress-corrosion specimens (anodes) and unstressed specimens (cathodes) of the J-1 alloy. All electrical leads were insulated and an insulating layer of Scotch Electrical Tape No. 33 was applied to the specimen ends leaving only an area 0.5 inch long at the apex of the bend exposed to the solution. Specimens were tested at a deflection of 0.150 inch. From a theoretical calculation, this gives a stress value of 69,000 psi. Duplicate specimens were solution-annealed for 24 hours at 650°F and water-quenched and then tested to determine if the measurements of corrosion currents were reproducible.

e. Effect of Stress on Corrosion Currents

A series of three specimens was run to determine if corrosion currents generated during testing were dependent upon stress level. The three specimens were all machined from the same production lot and were solution-annealed at 650°F for 24 hours and water-quenched. The specimens were stressed to deflections of 0.130 inch (60,000 psi), 0.150 inch (69,000 psi), and 0.165 inch (78,000 psi), respectively. Corrosion currents were measured in the standard manner.

f. Effect of Surface Preparation
on Corrosion Currents

Two specimens were tested to substantiate the belief that uniformity of surface preparation was a critical variable. One specimen

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of low iron level was solution-annealed for 24 hours at 650°F and water-quenched. Surface preparation was deliberately incomplete and consisted only of abrasion in random directions with 400-grit silicon carbide paper which was just sufficient to partially remove the oxide layer formed during heat treatment. The second specimen received an identical heat treatment but was prepared using normal metallographic techniques. The specimen was then exposed to normal laboratory air for 400 hours in the unstressed condition before exposure to standard stress-corrosive conditions.

g. Effect of Creep on Stress-Corrosion Susceptibility

A specimen which had been subjected to the standard 650°F, water-quench heat treatment was stressed to a deflection of 0.168 inch (78,000 psi) and allowed to stand in vacuum for 400 hours. The specimen was then exposed to standard test conditions.

h. Effect of Constant Loading Techniques on Corrosion Currents

Several specimens were run under conditions of constant load rather than constant deflection to determine if the method of loading had any effect on the curves of corrosion currents plotted against time. Two specimens were machined to final dimensions of 5 x 0.500 x 0.040 inches. One specimen was heat treated at 650°F for 24 hours and furnace-cooled, while the second was given a 5% cold-rolling operation followed by an 800°F solution-anneal with water quenching. Both specimens were placed in solution on supports four inches apart and loaded in their centers with a dead weight sufficient to obtain a stress level of 45,000 psi. All parts of the apparatus were non-metallic to prevent stray galvanic current generation. Corrosion currents were measured against unstressed cathodes of the J-1 alloy.

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i. **Microscopic Observations and Motion Pictures**

All runs made, with the exception of the constant load
determinations mentioned immediately above, were observed microscopically
and some were recorded by motion picture microscopy techniques at magnifi-
cations of 40x and 30x. A 16 mm "Auricon" sound motion picture camera was
mounted with a beam splitter directly onto the microscope as shown in Fig. 1.
The Motion Picture Division of the Department of Photography of The Ohio
State University assisted in the photography.

j. **The Effect of pH on Stress-Corrosion
in Salt-Chromate Solutions**

Several specimens were prepared with single-grain boundaries
oriented nearly transversely across the specimens. Small notches were
filed in the grain boundaries at the specimen edges to insure crack initia-
tion at these points. Specimens were produced with furnace-cooling and
with water-quenching to promote intergranular or transgranular cracking,
respectively. Both types of specimens were exposed in the standard solu-
tion of 40 g NaCl and 40 g K_2CrO_4 per liter of water (pH = 9.0) and in a
solution of 35 g NaCl and 20 g K_2CrO_7 per liter of water (pH = 3.5) to
determine if pH had any effect on the type of cracking.

k. **Effect of Variables on Type
of Stress-Corrosion Failure**

In order to understand the mechanisms of both transgranular
and intergranular failure more fully, a final series of experiments was
undertaken. Six specimens of each production lot were prepared by solution-
annealing at 600, 300, and (after a 5% cold rolling operation) $900^{o}F$ for
24 hours. Three specimens heated at each temperature were furnace-cooled

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and three were water-quenched. In this manner, the effects of iron content, grain size, and cooling method were all introduced as variables. All specimens were stressed at a deflection of 0.150 inch (69,000 psi) in the standard salt-chromate solution. Microscopic observations, measurements of corrosion currents, and determinations of sounds were made simultaneously to be utilized in the analysis of results.

$l.$ Hardness and Impact Resistance Values

To further supply a basis for mechanisms of the two types of stress-corrosion cracking, hardness and impact resistance measurements were made on one specimen in the $650^{\circ}F$ furnace-cooled condition and one in the high temperature, strain-annealed, and water-quenched condition.

D. RESULTS AND DISCUSSION

1. Study of Metallurgical Structure

Figure 3 shows the as-received structure of the two lots of alloy used in the investigation. The air cooling after hot extrusion promotes the slight precipitate of $Mg_{17}Al_{12}$ at the grain boundaries. Solid solution microsegregation is exhibited in both specimens as the precipitated "banding" effect shows and is more pronounced in the alloy with high iron content. Grain size was determined to be ASTM No. 12 by use of the ASTM non-ferrous grain size standard charts.

Figure 4 shows the structure of Lot No. 45 (low iron content) after solution-annealing for 24 hours at $650^{\circ}F$ followed by furnace-cooling or water-quenching. It can be noted that a heavy precipitate of $Mg_{17}Al_{12}$ exists in the furnace-cooled specimen. Grain size is still ASTM No. 12.

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No change in structure was noted after the 300 and 900°F heat treatments except that grain size increased with annealing temperature. At 800°F, grain size was ASTM No. 4, while a 900°F treatment following a 5% cold-rolling operation produced specimens with single or bi-crystals across their width. The only difference between specimens of the two lots which received identical heat treatments was a heavier grain boundary precipitate in the lot with higher iron content

2. Resolution of Sound Associated
   With the Cracking Process

Using the sensitive sound detection apparatus described previously, it was determined early in the investigation that noise was associated with the stress-corrosion cracking. The possible causes were considered to be evolution and collapse of microbubbles of hydrogen or actual mechanical fracture. Unstressed specimens in the $NaCl-K_2CrO_4$ solution produced a similar noise so that hydrogen evolution was thought to be the cause. Support of this idea was found in an identical noise produced by the evolution of hydrogen from zinc metal in hydrochloric acid. The noise of hydrogen evolution from a general corrosive attack on the specimen was eliminated by insulating the entire specimen except for a 0.500-inch length at the area of maximum stress. The noise of hydrogen evolution from the crack was negligible when the general evolution of hydrogen was thus eliminated. In later work it was noted that a loud crackling noise was produced during stress-corrosion of specimens which were susceptible only to transgranular cracking. This noise was duplicated by mechanically stressing to failure a specimen which was susceptible to transgranular failure and failed in a brittle manner. No sound was produced by stressing with identical

techniques an intergranular-prone specimen which failed only after considerable elongation. This sound of mechanical fracture is considered an important factor in the hypothesis concerning a mode of transgranular failure which will be discussed in a later section.

3. Evaluation of Changes in
   Electrical Resistance

The technique of measuring changes in electrical resistance has been used in recent years to obtain large amounts of data rapidly on uniform corrosion rates for long, thin specimens. The idea should be applicable to stress-corrosion testing where the effective cross section is rapidly decreasing and thus the resistance of the specimen is rapidly increasing. The apparatus used in this work is shown schematically in Fig. 5. Measurements of the voltage drop across the standard 1.000-ohm resistance is equivalent to an extremely accurate measurement of the current flowing in the system. The measured voltage drop across the specimen divided by the current then gives the resistance of the specimen in precise terms. It was found that an extremely high ratio of length to area is required for accurate reproducibility. The required ratio is impractical for the constant deflection technique used in these experiments and this technique was thus abandoned.

4. Measurements of Corrosion Current
   as a Test Method

Results from this technique appear extremely promising. The results of the two specimens with identical heat treatments which were stressed to the same level of 69,000 psi are shown in Table 2. The reproducibility is excellent and, on the basis of this experiment, measurements of corrosion currents were used extensively.

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5. Effect of Stress on Corrosion Currents

Corrosion currents which are generated by the action of stress-corrosion are dependent upon the stress level in the plastic range. Figure 6 shows a curve of corrosion currents plotted against time for three specimens with nominal stress levels of 60,000, 69,000, and 78,000 psi. As the stress is increased, the cracking initiates more quickly, the corrosion current reaches a higher maximum, and the specimen fails to completion more quickly.

6 Effect of Surface Preparation
on Corrosion Currents

A specimen was exposed with deliberately incomplete surface preparation and one was allowed to stand unstressed in normal laboratory air for 400 hours before exposure to test conditions. In both cases the corrosion currents generated were erratic and not reproducible, while excessive pitting resulted. This indicates that the scratches and oxide film layer cause a complex electrochemical system which cannot be analysed by conventional techniques. The results also emphasize the importance of proper surface preparation.

7. Effect of Creep on Stress-Corrosion
Susceptibility

The specimen which was stressed to a deflection of 0.160-inch (78,000 psi) in vacuum for 400 hours prior to testing did not initiate a crack after 30 minutes of exposure. The specimen and holder were then removed from solution and the stressing screw was loosened. Measurement of the specimen then showed that a permanent deflection of 0.102-inch had been imparted by the long stressing period. This indicates that creep had been operative to reduce the stress below a value at which stress-corrosion could occur under conditions of the test.

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8. Effect of Constant Loading Techniques
on Corrosion Currents

Stressing under constant load conditions subjects the specimens
to a more severe test than does a constant deflection technique. In the
constant deflection method, stresses begin at some low level, quickly reach
a maximum as the specimen begins to fail, and then rapidly drop off to zero
as the stresses are relieved by the widening crack. Constant load conditions
produce a situation where the stress level is constantly increasing as the
cross section of the specimen decreases. Constant deflection techniques
were used in the majority of this work since they permit easier microscopic
examination Results from specimens heat treated at 650 or 800°F and
stressed under conditions of constant load showed a steady increase in
corrosion current from zero to a maximum value which was reached at the time
of completion of cracking. The specimen heated at 650°F and furnace-cooled
failed in an intergranular manner and showed a regular increase of corrosion
current with time to a maximum of 25 micro-amperes. The specimen which was
given a 5% cold-rolling operation followed by heat treatment at 800°F and
a water-quenching failed transgranularly and the curve of corrosion current
versus time showed several large irregularities which seemed to correspond
with the advance of the crack tip across grain boundaries. The maximum
value of corrosion current for this specimen was 40 micro-amperes. From
these results, it is concluded that the curve of corrosion currents reaches
a maximum at the time when stresses acting upon the specimen are at a maximum.

9. Microscopic Observations and Motion Pictures

The microscopic observations, some of which were preserved in the
form of a motion picture, were very important in the attempts made to

understand the mechanisms of stress-corrosion. Both transgranular and intergranular cracks were observed. The appearance of twins as the stress concentration changed and the appearance of slip lines were recorded on film as well.

The important limitation involved in microscopic examination is that the observation is necessarily restricted to surface phenomenon. The situation in the interior of the material is unknown. However, as will be explained later, the use of audio and electrical techniques in conjunction with microscopic techniques is thought to permit a three dimensional analysis. For these reasons, an observed plastic deformation "shock wave" which propagated in advance of the crack tip is believed actually to be an indication of crack progress beneath the surface which then suddenly breaks through the surface layer to appear as a large step in the crack advance. This assumption is based on continuous corrosion current measurements and audible sounds.

10. The Effect of pH on Stress-Corrosion in Salt-Chromate Solutions

Results of the large grained specimens which were exposed to both NaCl-K_2CrO_4 (pH = 9.0) and NaCl-K_2CrO_7 (pH = 3.5) solutions indicate that specimens with large grain size always fail transgranularly. Even when cracking was initiated by pre-notching the specimen at a grain boundary which essentially ran at right angles across the specimen, cracking would deviate from the grain boundary and proceed transgranularly. This effect was noticed in both solutions.

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11. Effect of Variables on Type of
    Stress-Corrosion Failure

Microscopic observations, measurements of corrosion current, and audio pickup were all used simultaneously since prior experience indicated that correlation of these three test methods permitted a reliable analysis of the total phenomenon.

The effect of each variable was evaluated by obtaining average values for the corrosion currents of three identical specimens with the same iron content, grain size, and cooling rate. Qualitative observations were made concerning the sound produced and the microscopic observations.

Table 3 presents a summary of all corrosion currents which were measured. Measurements were made at 20-second intervals throughout the run, but maximum values are considered to be most significant for the purpose of analysis. The percentage of transgranular failure was obtained by visually counting the number of grains which failed in a transgranular manner and dividing by the total number of grains across the specimen width.

Several significant trends were noted from this data. The specimens with the higher percentages of transgranular failure exhibited higher maxima in all cases. Percentage of transgranular failure increased with higher iron content, faster cooling rate, and larger grain size.

Although it is not shown by Table 3, corrosion currents of the specimens which failed in a predominantly intergranular manner were more reproducible throughout the run. It was noted that the curves for specimens which failed intergranularly were smooth and regular as shown in Fig. 7. However, Fig. 8 shows that rather severe fluctuations appear in a curve for

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predominately transgranular failure. For the purpose of illustrating this point, corrosion currents were read at intervals of 10 seconds to provide a more accurate analysis.

It was also noted that the time to failure in the transgranular crack-susceptible specimens was proportional to the number of grain boundaries crossed by the crack tip.

It was observed microscopically that intergranular cracks advanced at a fairly uniform rate. Transgranular cracks advanced in short bursts and appeared to halt temporarily when the crack tip reached a grain boundary. A crackling noise was detected continually during transgranular failure but the sound level varied considerably. During intergranular attack, sound was essentially absent in all cases. It appears that the fluctuations in corrosion current, the step-wise crack advance, and the variations in sound which are associated with transgranular cracking are complementary. Similarly, the smooth curves of corrosion current, the constant rate of crack advance, and the virtual absence of sound during intergranular failure seem to correspond with one another.

12. Hardness and Impact Resistance Values

Five determinations of hardness were made on one specimen which had failed in a transgranular manner and on a specimen which had failed in an intergranular manner. The average Knoop hardness value for the first was 82.3 and for the second was 58.2. Charpy impact testing of a specimen susceptible to transgranular cracking gave a value of 5.3 foot-pounds, while the same test of a specimen susceptible to intergranular failure gave a value of 7.2 foot-pounds. Both types of test indicate that material which fails transgranularly is inherently more brittle.

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13. General Discussion of Results Applied
to a Proposed Mechanism for Transgranular
Stress-Corrosion

The results of this investigation support the previously advanced
theory which indicates that different mechanisms exist for transgranular
and intergranular stress-corrosion of the J-1 alloy in the salt-chromate
solution. Differences in structure contribute to this variation in types
of attack. The differences between corrosion current curves substantiate
the distinction between types of attack. The sound which is associated
with transgranular failure and is absent during intu-granular attack further
emphasizes the differences of mechanisms. The relatively constant rate of
crack propagation in specimens failing in an intergranular manner as com-
pared to the clserved temporary cessation of crack advance at grain bound-
aries and the step-wise propagation through the grains during transgranular
failure are also significant. Electrochemistry and stress are each con-
sidered to be of importance in both types of cracking.

It is believed that stress acts only to pull the metal apart dur-
ing intergranular stress-corrosion, while electrochemical attack due to the
potential difference which exists between grain boundaries and grain
interiors causes the rapid failure. The absence of sound, which is associated
with mechanical failure, supports this idea.

It is not presumed that this investigation is positive evidence
of a detailed theory of transgranular stress-corrosion. However, several
noteworthy conclusions have been reached which strongly indicate a possible
mechanism. Electrochemistry must play an important role in the transgranular
attack, as indicated by the corrosion currents generated. The fluctuations

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in corrosion current indicate a discontinuous rate of propagation, as do
the variations in the associated noise level. The noise produced during
failure is also considered indicative of a predominantly mechanical fail-
ure. This mechanical failure proceeding in a discontinuous manner could
cause the fluctuations in corrosion current by exposing fresh anodic metal
at varying rates. The brittleness associated with the specimens which
are susceptible to transgranular failure can be assocated with a blocking
effect on dislocation movement which prevents plastic deformation. The
fact that water-quenching and high iron contents have been associated with
both transgranular attack susceptibility and a segregation of FeAl pre-
cipitation within the grains suggests that this sub-microscopic precipi-
tate may be responsible for the hypothesized dislocation blocking effect.
This precipitate has been reported to form on the basal plane. It is
possible that the iron present in the alloy may distort the lattice and
thus provide the activation energy necessary to aid the passage of
magnesium into solution as ions.

In summary, the mechanism of transgranular attack would appear
to be a discontinuous one of alternate stages of mechanical failure and
electrochemical attack with the mechanical stage predominating. The func-
tion of electrochemical attack seems to be formation of trenches until a
high stress concentration is reached. At that point, the mechanical fail-
ure occurs in a brittle manner for a finite distance until some mechani-
cally strong obstruction such as a grain boundary is reached. Electro-
chemical dissolution then removes the obstruction and the brittle mechanical
stage repeats itself. The brittle behavior is attributed to blocked dis-
location movement, caused by the FeAl precipitate.

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Table 1. Spectrographic Analyses of Materials

Lot No.	%Al	%Ca	%Cu	%Fe	%Mn	%Ni	%Pb	%Si	%Zn
43	6.0	< 0.01	0.003	0.002	0.16	< 0.001	< 0.001	< 0.01	0.72
44	6.7	< 0.01	0.006	0.005	0.20	< 0.001	< 0.001	< 0.01	0.79

Table 2. The Reproducibility of Corrosion Currents
Generated by Two Identical Specimens

Time (secs.)	Corrosion Currents (uA)	
	Specimen No. 1	Specimen No. 2
0	0.0	0.0
20	1.0	0.9
40	1.2	1.2
60	1.5	1.4
80	2.0	2.2
100	2.5	3.5
120	3.9	4.2
140	5.0	5.1
160	6.0	5.9
180	6.7	6.7
200	7.3	7.5
220	7.9	7.9
240	7.9	8.1
260	8.0	8.0
280	7.4	7.9
300	7.5	6.5
320	6.9	6.4
340	5.9	6.1
360	4.8	5.3
380	3.5	2.5
400	1.6	1.3
420	1.0	0.8
440	-0.9	-1.0

Table 3. The Effects of Iron Content, Grain Size, and Cooling Rates
on Corrosion Currents Generated During Stress-Corrosion

| % Trans-granular Failure	Heat Treatment*	ASTM Grain Size	% Iron	Maximum Corrosion Current (u-A)
35	650°F, FC	12	0.002	8.1
40	650°F, WQ	12	0.002	9.9
60	650°F, FC	12	0.005	11.6
65	650°F, WQ	12	0.005	12.2
60	800°F, FC	4	0.002	12.6
65	800°F, FC	4	0.005	14.0
75	800°F, WQ	4	0.002	14.5
80	800°F, WQ	4	0.005	14.7
90	SA, 900°F, FC	bi-crystal	0.002	14.0
95	SA, 900°F, FC	bi-crystal	0.005	14.6
95	SA, 900°F, WQ	bi-crystal	0.002	15.2
100	SA, 900°F, WQ	bi-crystal	0.005	15.6
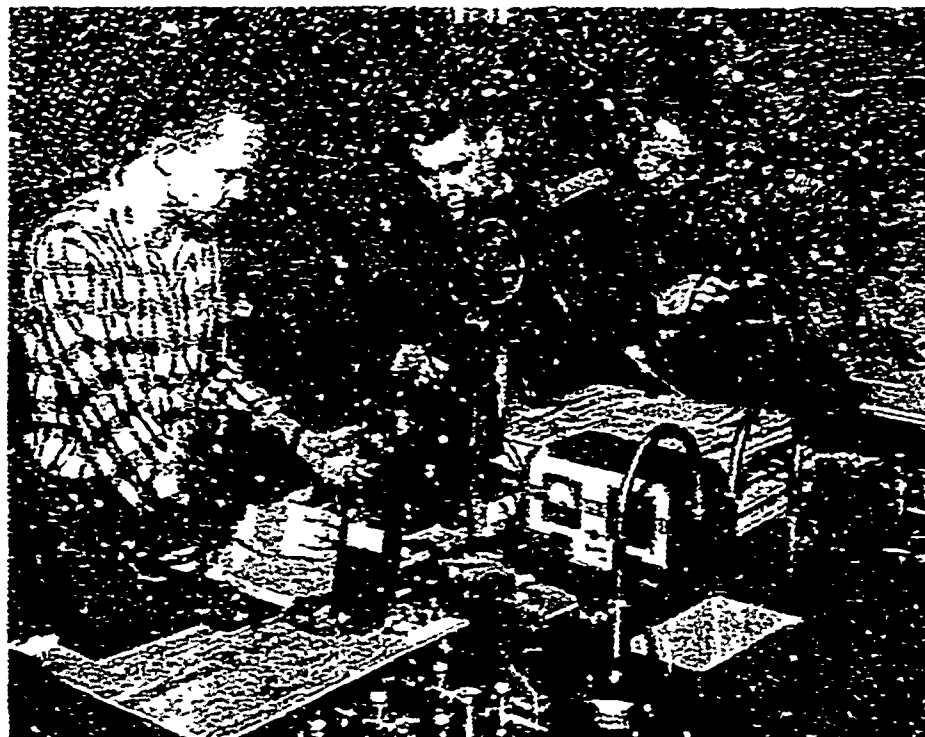
Fig. 1. Equipment for the Study of Stress-Corrosion

Foreground, left to right: Micro-ammeter
                         Audio probe on ringstand
                         Audio amplifier

Background, left to right: Light source
                          Micrometer stage with solution
                             container
                          Microscope with beam-splitter
                          "Auricon" motion picture camera
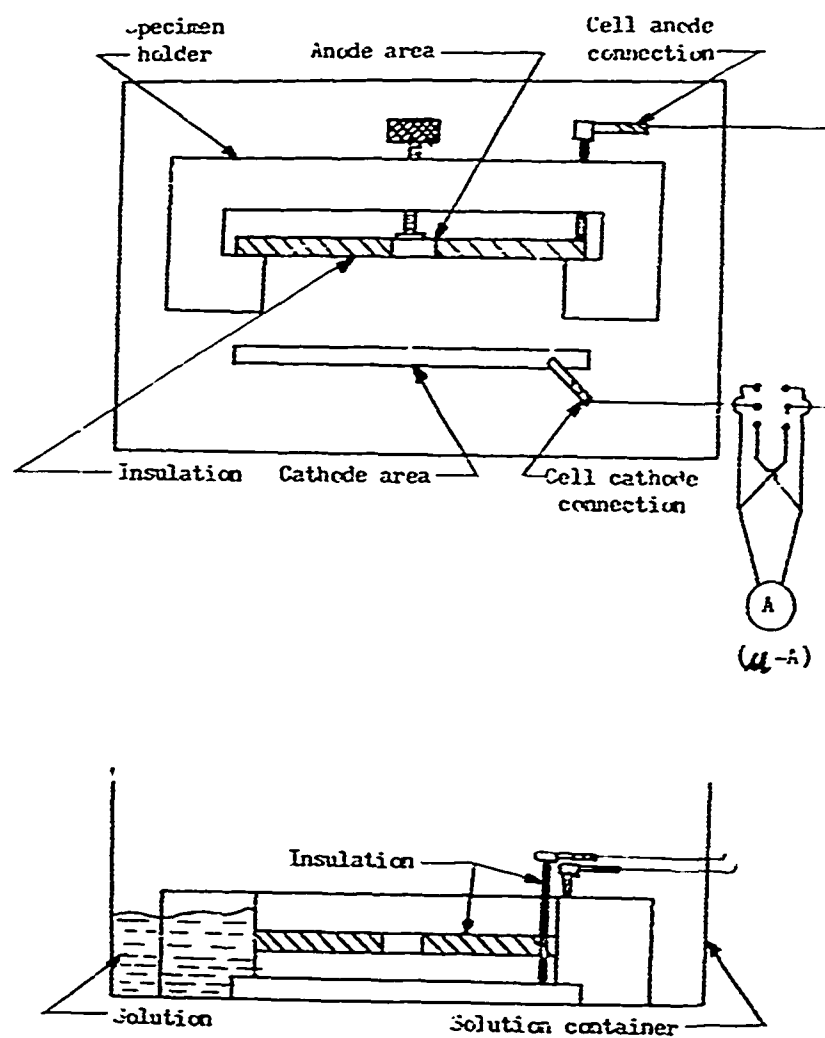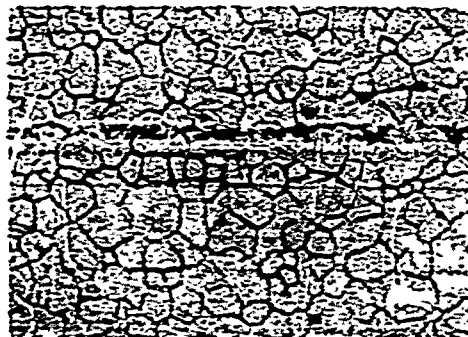   Sound recording equipment

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Specimen
holder

Anode area

Cell anode
connection

Insulation   Cathode area   Cell cathode
connection

$(\mu-A)$

Insulation

Solution   Solution container

Fig. 2. Specimen, Holder, and Solution Container with
Electrical Connections

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Picric-Acetic   Lot Number 43   500x
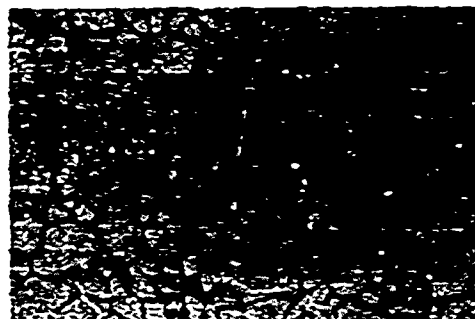

Picric-Acetic   Lot Number 44   500x

Fig. 3.   Microstructures of As-Received Alloys

Picric-Acetic   Water Quenched   500x

Picric-Acetic   Furnace Cooled   500x

Fig. 4. Microstructures Resulting From Two Cooling
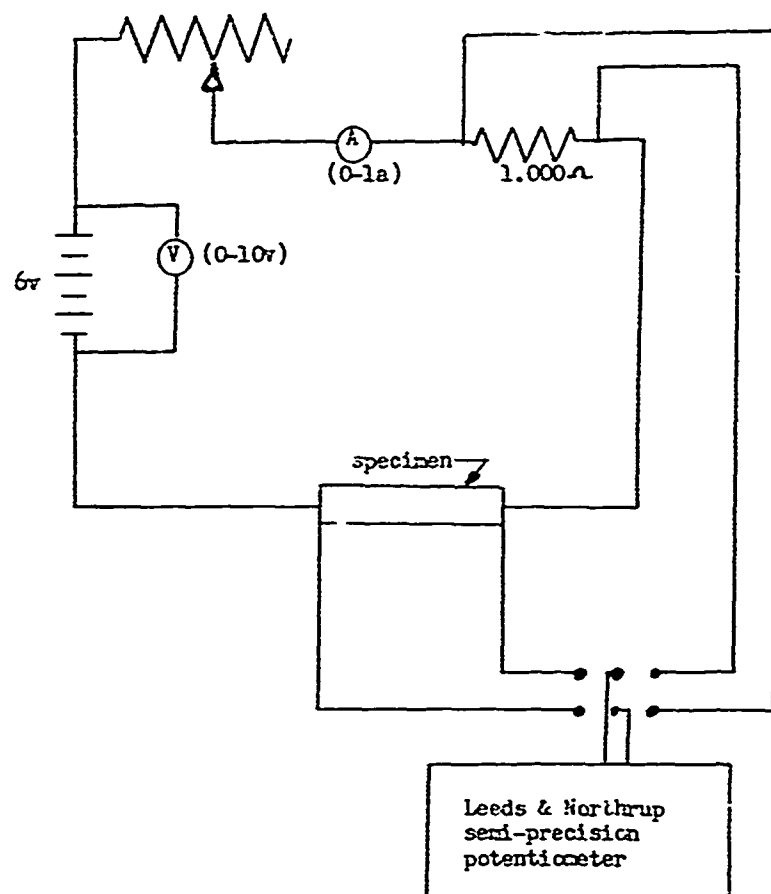Rates From a 650°F Solution Anneal

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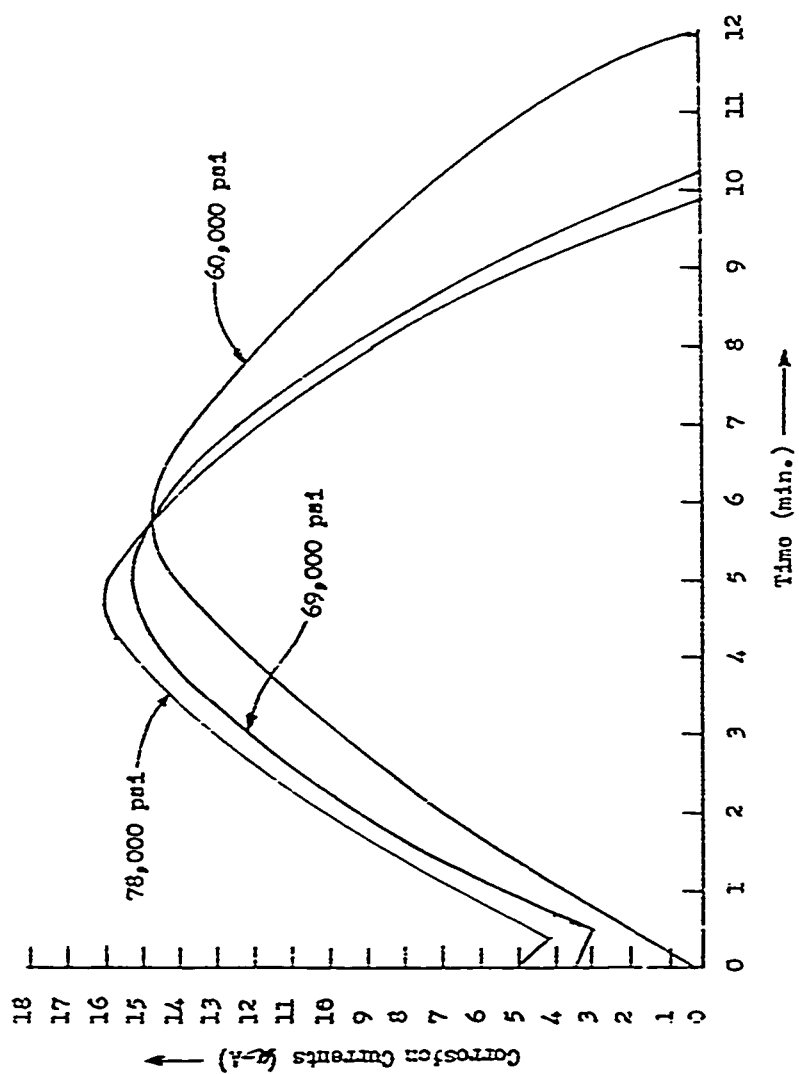Fig. 5. Apparatus for Measurement of Electrical Resistance

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Fig. 6. Effect of Plastic Deformation on Corrosion Currents
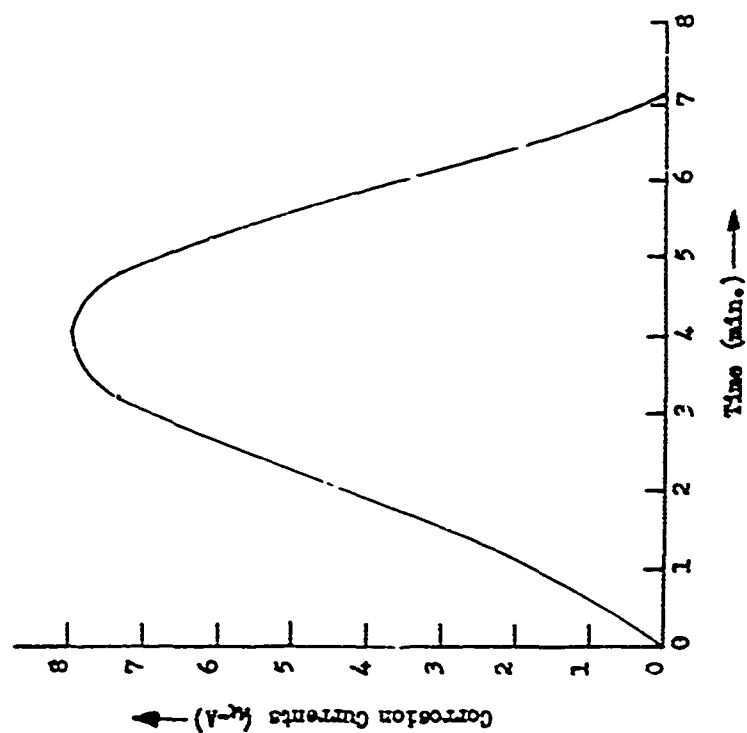
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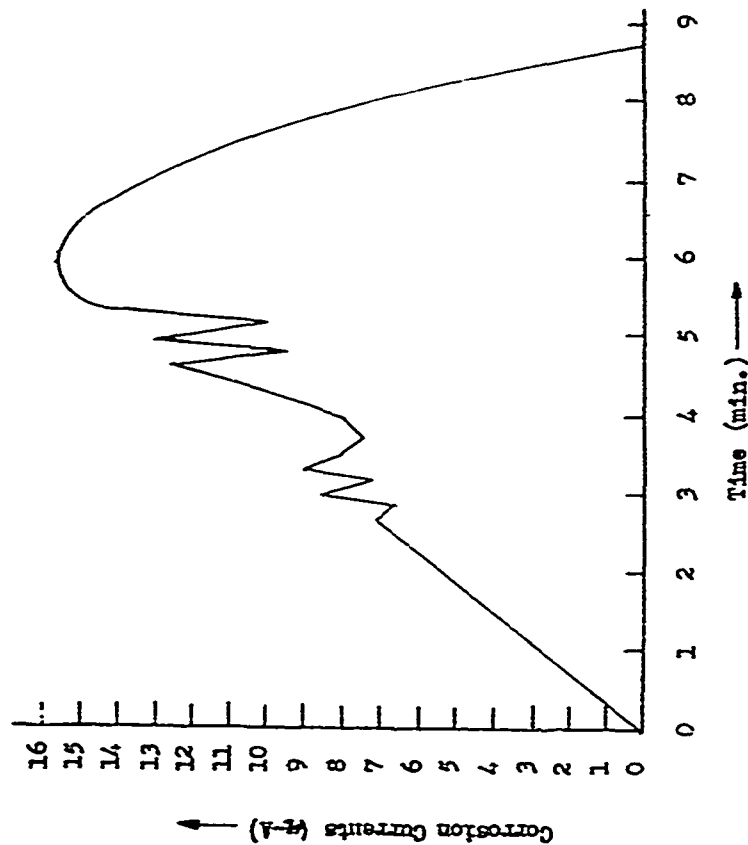Fig. 7. Corrosion Currents Versus Time for Typical Interpranular Failure

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Fig. 8. Corrosion Currents Versus Time for Typical Transgranular Failure

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PART II. STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEEL BY 400°F WATER CONTAINING NaCl

A. INTRODUCTION

This section contains work accomplished during the last quarter on the stress-corrosion cracking of austenitic stainless steels. Experiments were performed in which the "wedging action" of corrosion products was examined. Measurements of resultant stresses were made by x-ray and mechanical techniques.

Further work was done by electron microscopy and transmission techniques to study some of the structural aspects of the stress corrosion cracking technique.

Also, a brief review of previous work is presented. Stress-corrosion data obtained for materials other than austenitic stainless steels were reported in Progress Report Nos. 11, 12, and 19.

B. SUMMARY AND CONCLUSIONS

Stainless steels exposed to sodium chloride containing waters at elevated temperatures develop large quantities of insoluble corrosion products.

The insoluble corrosion products, when confined, may produce stresses sufficiently high to promote stress-corrosion crack initiation and propagation in annealed austenitic stainless steel specimens.

Stresses induced by the "wedging action" may be additive to internal and/or applied stresses.

Mechanical methods and x-ray techniques can be used to measure the stresses induced by the "wedging action" of confined corrosion products.

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C. RESULTS AND DISCUSSION

Results to date on "wedging action" have shown that non-soluble corrosion products play a significant role in the initiation and propagation of stress-corrosion cracks in the austenitic stainless steels when these materials are exposed to NaCl solutions at 400°F. The nature of the products causes a "wedging action" in confined regions such as pits and cracks, producing tensile stresses at the base of cavity which are additive to the applied stresses. This wedging effect is probably the major source of stress in the case where cracking occurs under very low applied stresses, i.e., cracking of the austenitic stainless steels at applied stress of 2000 psi.

Measurement of the stresses developed by the products is in progress. Changes in lattice parameter due to the introduction of elastic stains in the specimen have been recorded by back-reflection x-ray examination in which stresses are calculated from line displacement.

A mechanical method, based on the deflection of a titanium alloy beam, was also used in which corrosion products from a stainless steel wedge were made to act in a direction perpendicular to the titanium beam axis. In other words, the wedge behave. in the same manner as the screw in Fig. 2 of Technical Report No. 2. Stresses are then calculated from the amount of deflection in the titanium beam as a function of exposure time.

This study will require additional research. Experiments will be necessary to determine the identity and properties of the corrosion product, and to learn more about its growth in confined regions before the maximum forces exerted can be determined.

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REPORTS AND PUBLICATIONS

1. Progress

Report No.	Period	Date
1	February -April	May 19, 1956
2	May-July	August 24, 1956
3	August-October	Nov. 15, 1956
4	November-January	February 7, 1957
5	February-April	June 5, 1957
6	May-July	July 31, 1957
7	August-October	November 26, 1957
8	November-January	February 10, 1958
9	February-April	May 12, 1958
10	May-July	August 1, 1958
11	August-October	November 24, 1958
12	November-January	February 25, 1959
13	February-April	May 20, 1959
14	May-July	August 14, 1959
15	August-October	November 27, 1959
16	November-January	March 10, 1960
17	February-April	May 24, 1960
18	May-July	September 9, 1960
19	August-October	November 28, 1960
20 (Final)	November-January	January 31, 1961

2. Technical and Publications

TR-1 (Reprint)- "The Effect of NO, HNO_2, and HNO_3 On Corrosion of Stainless Steel by H_2SO_4," McKinnell, Lockwood, Speiser, Beck and Fontana; Corrosion, 14, January 1958, pp. 27-30.

Special Paper - "Sorption of Some Diatomic Gases on Stainless Steel and Iron Surfaces and Its Relation to Passivity." Zeits. f. Electrochem., 62 (6/7), 733, 1958.

TR-2 - "Mechanism of Stress Corrosion of Austenitic Stainless Steels in High Temperature Chloride Waters," Staehle, Beck, Fontana, April 1958.

TR-3 (Preprint) - "Influence of Nickel on Intergranular Corrosion of 18% Chromium Steels," Upp, Beck, Fontana. Trans. ASM; pp. 759-772, July 1958.

TR-4 (Reprint) - "Mechanism of Stress Corrosion of Austenitic Stainless Steels in Chloride Waters," Staehle, Beck and Fontana, Corrosion, pp. 51-59, July 15, 1959.

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Special Paper - "Stress Corrosion Cracking of Austenitic Stainless Steels in High Temperature Chloride Water." and "Stress Corrosion of Austenitic Stainless Steels by Hot Salts,", Met. Soc. Conferences, Vol. 4, Physical Met. of Stress Corrosion Fracture, 1959.

TR-5 - "Anodic Polarization Behavior of Iron-Nickel Alloys in Sulfuric Acid Solutions," Economy, Speiser, Beck, and Fontana, August 1960.

TR-6 (Preprint) - "Rapid Intergranular Oxidation of 18-8 Stainless Steels by Oxygen and Sodium Chloride at Elevated Temperatures," Pickering, Beck, Fontana, Trans. ASM, pp. 793-803, January 1961.

(Film on File) - Motion Picture Film on "Stress Corrosion of 18-8 Stainless Steel by NaCl Containing Waters at 400°F," (1959).

Investigator _____F. H. Beck_____ Date _____

Supervisor _____M. T. Fontana_____ Date _____

For The Ohio State University Research Foundation

Executive Director _____Daniel Walpert_____ Date 4/16/61

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